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ISOMER SELECTION OF 1,6-DIAMINOHEXANECADMIUM(II) TETRACYANONICKELATE(II) FOR m- AND p-TOLUIDINE.

FORMATION OF 1,6-DIAMINOHEXANECADMIUM(II) TETRACYANONICKELATE(II)-m-TOLUIDINE(1/1) INCLUSION COMPOUND AND BIS(p-TOLUIDINE)-1,6-DIAMINOHEXANECADMIUM(II) TETRACYANONICKELATE(II) COMPLEX

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Under substantially the same preparation conditions applied to the *m*- and the *p*-isomers of toluidine with the aqueous solution containing cadmium(II) chloride, potassium tetracyanonickelate(II), 1,6-diaminohexane, and some additives, the *m*-isomer gives an inclusion compound 1,6-diaminohexanecadmium(II) tetracyanonickelate(II)-*m*-toluidine(1/1) as well as the *o*-isomer does, whereas the *p*-isomer forms a metal complex bis(*p*-toluidine)-1,6-diaminohexanecadmium(II) tetracyanonickelate(II).

In the course of our investigations to develop three-dimensional metal complex hosts able to accommodate aromatic guest molecules with bulky substituents, we have derived Hofmann-α,ω-diaminoalkane-type hosts from the original Hofmann-type $Cd(NH_3)_2Ni(CN)_4$ by replacing the pair of ammine ligands by the α,ω-diaminoalkane ligands behaving ambidently.[1)] The inclusion compounds have the general compositional formula $Cd(\alpha,\omega\text{-diaminoalkane})Ni(CN)_4 \cdot nG$ where G refers to a guest aromatic molecule and the value of n (=1-2) depends on the guest.[1)] Among them the crystal structures have been determined for the Hofmann-dabn-type (dabn=1,4-diaminobutane) 2,5-xylidine,[2)] pyrrole, aniline, and N,N-dimethylaniline inclusion compounds,[3)] and for the Hofmann-dahxn-type (dahxn=1,6-diaminohexane) *o*-toluidine inclusion compound.[4)]

In order to clarify the structural features of the Hofmann-dahxn-type series, further attempt to prepare Hofmann-dahxn-type inclusion compound with the *m*- or the *p*-isomer of toluidine was carried out under the same conditions as that applied to the *o*-isomer compound except that the *m*- or *p*-isomer was used in place of the *o*-isomer.[4)] The products obtained as yellow crystals were analyzed to ascertain the chemical compositions. Although the *m*-isomer compound gave the stoichiometric coefficient n=1 in the general formula $Cd(C_6H_{16}N_2)Ni(CN)_4 \cdot nCH_3C_6H_4NH_2$ as well as the *o*-isomer one, for the *p*-isomer compound the value n=2 was obtained. This suggested that the *m*-isomer compound may have the structure similar to that of the *o*-isomer one whereas the *p*-isomer compound would take a different structure from the compound with the *o*- or the *m*-isomer. Another problem was the splitting of the CN stretch IR-band into a doublet (2145 and

2120 cm^{-1}) for the *p*-isomer compound in spite that the singlet (*ca*. 2150 cm^{-1}) was observed for the *o*- and *m*-isomer compounds. The crystal structure analyses of both the compounds dissolved the problems.

The crystals of Cd(dahxn)$Ni(CN)_4 \cdot$*m*-$CH_3C_6H_4NH_2$ (**1**) and [Cd(*p*-$CH_3C_6H_4NH_2)_2$-$(C_6H_{16}N_2)$]$Ni(CN)_4$ (**2**) were grown up by the method described previously.$^{4)}$ Found for **1**: C, 40.73; H, 5.15; N, 19.57%. Calcd for $C_{17}H_{25}N_7CdNi$: C, 40.95; H, 5.05; N, 19.66%. Found for **2**: C, 47.2; H, 5.5; N, 18.6; Cd, 19.0; Ni 10.0%. Calcd for $C_{24}H_{34}N_8CdNi$: C, 47.59; H, 5.66; N, 18.50; Cd, 18.56; Ni, 9.69%. Each single crystal of **1** and **2** was coated with epoxy resin in order to prevent spontaneous decomposition under ambient condition during the intensity data collection, which was carried out on a Rigaku AFC-A6 automated four-circle diffractometer using a graphite-monochromated Mo Kα radiation (λ=0.71069 Å). The crystal data are as follows:

1, $Cd(C_6H_{16}N_2)Ni(CN)_4 \cdot C_7H_9N$, F.W.=498.55; triclinic, $P\bar{1}$; a=9.726(2), b=7.598(1), c=7.177(1) Å; α=89.56(1), β=98.81(1), γ=84.30(1)°; U=521.3(2) $Å^3$; Z=1; D_x=1.62, D_m=1.61 g cm^{-3}; number of reflections used: 3526.

2, $Cd(C_6H_{16}N_2)(C_{14}H_{18}N_2)Ni(CN)_4$, F.W.=605.70; monoclinic, $P2_1/n$; a=12.107(3), b=10.117(2), c=12.471(3) Å; β=113.67(2)°; U=1399.0(6) $Å^3$; Z=2; D_x=1.44, D_m=1.45 g cm^{-3}; number of reflections used: 2616.

The setting of coordinates for **1** has been chosen for the sake of comparison with the structure of the *o*-toluidine inclusion compound Cd(dahxn)$Ni(CN)_4 \cdot$*o*-$CH_3C_6H_4NH_2$ (**3**) reported previously.$^{4)}$ The structures were solved by the heavy-atom method. At the present stage the conventional reliability indices R=0.038 and R=0.037 have been obtained for **1** and **2**, respectively.

The structure of **1** in Fig. 1 is essentially the same as that of **3**. Although the space group is different from that of **3**, the unit cell dimensions are similar to those of **3** except a small degree of distortion to the triclinic system in **1**: for **3** the space group P2/m, a=9.541(2), b=7.569(2), c=7.199(1) Å, β=100.3(1)°, U=511.5(2) $Å^3$. The dahxn ligand in the all-trans configuration bridges adjacent cyanometal complex networks at the Cd atoms. The network is bent at each Cd-N(cyano) junction to give a waved structure. The guest *m*-toluidine molecule is accommodated in the cavity formed between the adjacent cyanometal complex networks and surrounded by four dahxn "columns"; the center of the cavity, 1/2,1/2,0, is an inversion center. A difference between **1** and **3** is seen in the orientation of guest molecule. The *m*-toluidine in **1** is distributed statistically about the inversion center to show an apparent molecular shape like 1,4-diamino-2,5-dimethylbenzene but the occupancy factor of each substituent group is 0.5.

The structure of **2** is remarkably different from those of **1** and **3**. Although the dahxn ligand in **2** behaves ambidently to the Cd atom as well as those in **1** and **3**, the *p*-toluidine molecule in **2** is not a guest but a unidentate ligand coordinating at the amino-nitrogen to the Cd atom, and a pair of the unidentate ligands coordinate in a trans configuration. The six-coordination of the Cd atom is accomplished by further ligation of two N-ends of $Ni(CN)_4$ moieties as shown in Fig. 2. Thus the two-dimensional network is built of the catena-μ-linkages of -Cd-dahxn-Cd-dahxn- chain, in which the skeletal configuration of dahxn is cis-trans-cis, along the c-axis and -Cd-NC-Ni-CN-Cd- chain along the b-axis, both the

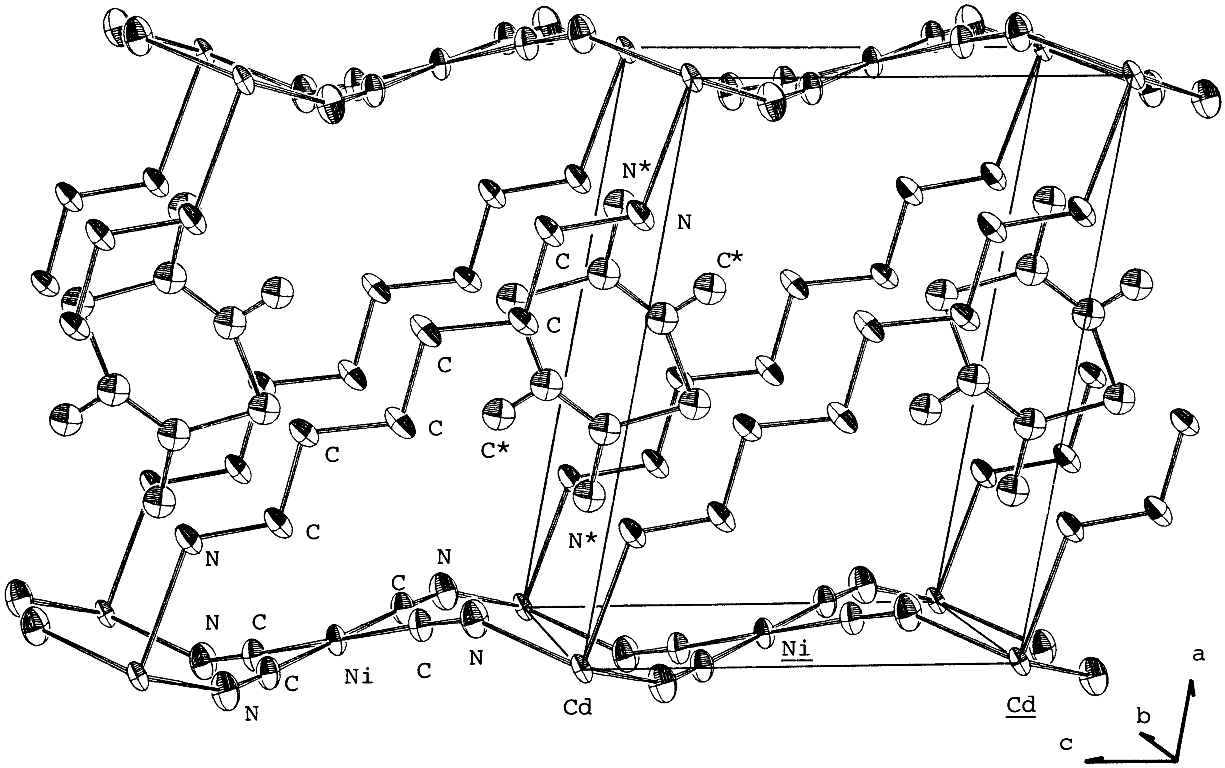

Fig. 1. A perspective view of Cd(dahxn)Ni$(CN)_4$•m-$CH_3C_6H_4NH_2$. Two unit cells along the c-axis are shown; hydrogen atoms are omitted; Cd at 0,0,0 and Ni at 0,0.5,0.5; each of the C* and N* has the occupancy factor of 0.5, respectivley; the dahxn ligand bridges two corners of a unit cell approximately on the ac-plane.

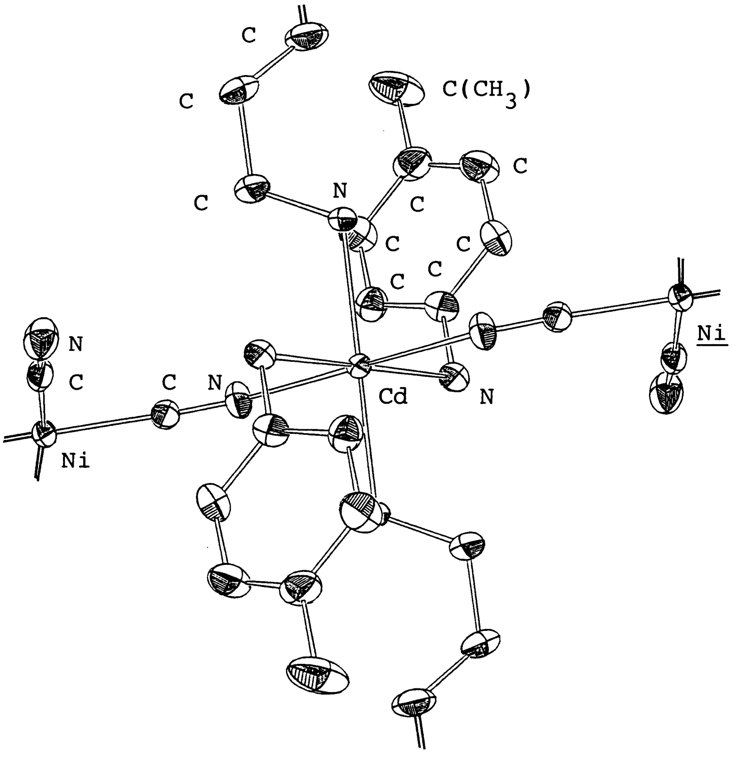

Fig. 2. Coordination structure about the Cd atom in [Cd(p-toluidine$)_2$(dahxn)]-Ni$(CN)_4$; Cd at 0.5,0.5,0.5, Ni at 0.5,0,0.5, Ni at 0.5,1,0.5.

chains are interconnected at each Cd atom. Thus the compositional formula should be written as [Cd(p-toluidine)$_2$(dahxn)]Ni(CN)$_4$. With regard to the Ni(CN)$_4$ moiety, two CN groups are involved with the catenation but the rest two have free N-end. Since the molecular group of tetracyanonickelate(II) ion is lowered from the D_{4h} in **1** and **3** to D_{2h} in **2**, the CN stretch IR-band of the E_u mode in **1** and **3** should be splitted into a doublet of the B_{2u} and B_{3u} modes in **2**; qualitatively the 2145 cm^{-1} band is assigned to the bridging CN and the 2120 cm^{-1} one to the CN with free N-end.[5)] In the Raman spectra, **1** and **3** showed the doublet structure of the bands at 2143 and 2133 cm^{-1}, the A_{1g} and the B_{1g} modes in the D_{4h} symmetry, with an intensity ratio 2:1 but **2** gave the more splitted and lower-shifted doublet of the bands at 2128 and 2110 cm^{-1} assignable to the A_g and B_{1g} modes in the D_{2h} symmetry. The correlation of the molecular group of tetracyanonickelate(II) with the site and the factor groups in the crystal structures appears to be negligible within the spectral resolution range of ± 5 cm^{-1} for the IR and ± 3 cm^{-1} for the Raman bands.

Details about the crystal structures will be reported elsewhere with the discussion on the selectivity of the metal complex host for the three isomers.

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